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DESCRIPTION

GLASS FOR LASER PROCESSING

5 TECHNICAL FIELD

The present invention relates to a glass for laser processing that can be laser-processed through laser beam irradiation. Particularly, the present invention relates to a glass for laser processing whose composition is suitable for laser processing.

10

BACKGROUND ART

Recently, the technique of processing materials using laser beam energy has been developing gradually to cover the field of micro-processing.

15 In the processing technique using a mask pattern, the processable length has been extended to the range of nanometers that are further shorter than micrometers due to the progress of the patterning technique and the shortening of a laser wavelength.

20 On the other hand, direct processing using a laser also has been practiced in the range of micrometers in the case of processing metal and organic matters such as polyimide as a result of the progress in shortening of the wavelength and pulse width of laser beams.

25 Furthermore, processing such as perforating using a laser is shifting to ablation processing from thermal processing. Ablation is a phenomenon that the state of a material of an irradiation part shifts from melting to evaporation in a short period of time through irradiation of laser beams whose pulse width is very narrow. The level of thermal influence on the periphery of the beam irradiation part varies with an increase or a decrease in pulse width. In the case of processing using an ultrashort pulse laser that completes beam irradiation before thermal diffusion occurs, it is possible to
30 make precise minute holes, with hardly any heat-affected layer being generated.

However, many of the lasers that are used for actual processing employ pulse widths of at least the nanosecond order, which makes it impossible to avoid the thermal influence. Hence, a photochemical reaction
35 that is caused by ultraviolet rays is employed. Short-wavelength beams of a laser such as, for instance, an excimer laser have great energy per photon and therefore can cut a chemical bond that forms a molecular skeleton.

As described above, the selection of, for instance, the pulse width and wavelength of a laser beam to be used for irradiation conventionally has made it possible to carry out micro-processing. The study, however, has not progressed so much from the viewpoint of improvement of materials to be irradiated with a laser. Processing of glass that is a transparent material is important for optical application. In order to provide a glass suitable for laser processing, JP11(1999)-217237A proposes a technique for providing glass in which cracks tend not to occur by decreasing the laser processing threshold value through the introduction of silver into glass by ion exchange.

Glass containing a large amount of alkali metal allows silver ions to be introduced therein by a silver ion exchange. However, a phenomenon occurs in which silver ions are reduced in the vicinity of the glass surface and thereby are inhibited from diffusing into the glass. Hence, the effective laser processing region is limited to the vicinity of the glass surface and therefore it still is difficult to carry out processing of glass including processing of the inner part thereof, for instance, processing to make a through hole in a glass sheet. In addition, there is another problem that the ion exchange rate is low and it therefore is difficult to allow ions to reach the inner part of glass stably.

Moreover, glass for laser processing produced through the silver ion exchange contains a large amount of alkali metal or alkaline-earth metal and therefore has a high thermal expansion coefficient, which is a problem. Since heat is generated in a laser irradiation part during laser processing, the laser irradiation part and the vicinity thereof are deformed due to the stress caused by the difference in thermal expansion between them. When the thermal expansion coefficient is high, the size of a processing part measured during laser irradiation varies from that measured after laser irradiation. Hence, the dimensional accuracy of the processing part may deteriorate.

Furthermore, with respect to optical elements, it generally is desirable that the dimensional change that is caused by a temperature change be small. There also is a problem that such a dimensional change as described above may cause variations in the characteristics of optical elements.

DISCLOSURE OF THE INVENTION

In order to solve the above-mentioned problems, the present invention is intended to provide a glass for laser processing that has a low

laser processing threshold value as well as a low thermal expansion coefficient.

The glass for laser processing of the present invention is a glass that can be laser-processed by causing ablation or evaporation by laser beam energy absorbed therein. The glass for laser processing is characterized in having a composition that satisfies the following conditions:

$$60 \leq \text{SiO}_2 + \text{B}_2\text{O}_3 \leq 79 \text{ mol\%};$$

$$5 \leq \text{Al}_2\text{O}_3 + \text{TiO}_2 \leq 20 \text{ mol\%}; \text{ and}$$

$$5 \leq \text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Rb}_2\text{O} + \text{Cs}_2\text{O} + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} \leq 20 \text{ mol\%},$$

wherein $5 \leq \text{TiO}_2 \leq 20 \text{ mol\%}$.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic view showing an optical system used for measuring a laser processing threshold value of an example according to the present invention.

FIG. 2 is a diagram showing a composition range in which uniform glass can be produced in an example according to the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

A glass of the present invention can be processed by causing ablation or evaporation by laser beam energy absorbed therein. In the above, the term "ablation" denotes a phenomenon that the state of a material of an irradiation part shifts from melting to evaporation in a short period of time through irradiation of laser beams whose pulse width is very narrow.

The composition of the glass according to the present invention satisfies the following conditions:

$$60 \leq \text{SiO}_2 + \text{B}_2\text{O}_3 \leq 79 \text{ mol\%};$$

$$5 \leq \text{Al}_2\text{O}_3 + \text{TiO}_2 \leq 20 \text{ mol\%}; \text{ and}$$

$$5 \leq \text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Rb}_2\text{O} + \text{Cs}_2\text{O} + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} \leq 20 \text{ mol\%},$$

wherein $5 \leq \text{TiO}_2 \leq 20 \text{ mol\%}$.

Preferably, this glass for laser processing contains titanium in the form of an atom, colloid, or ion.

In the glass having the composition described above, SiO_2 or B_2O_3 is an oxide that forms a network of the glass, and it forms a skeleton of the glass. When the total amount of SiO_2 and B_2O_3 exceeds 79 mol%, the glass

is difficult to melt. The total amount, therefore, is preferably 79 mol% or less.

Furthermore, since Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O , MgO , CaO , SrO , or BaO , which is a modifier oxide, breaks part of the network structure of the glass, it is used for reducing viscosity to be obtained at high temperatures or decreasing the temperature gradient of viscosity. In order for this effect to be exhibited readily, it is preferable that the total amount of the modifier oxides be at least 5 mol%.

Al_2O_3 or TiO_2 is an intermediate oxide and can be present in the glass as either a network forming oxide or a modifier oxide according to the balance between SiO_2 or B_2O_3 , which is a network forming oxide, and Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O , MgO , CaO , SrO , or BaO , which is a modifier oxide. Particularly, TiO_2 is a component that is necessary for lowering the laser processing threshold value. It, therefore, is necessary that the content of TiO_2 be 5 mol% to 20 mol%. A content of TiO_2 of less than 5 mol% results in a high laser processing threshold value, which is not preferable. On the other hand, a content of TiO_2 exceeding 20 mol% results in a high thermal expansion coefficient, which is not preferable.

When the total amount of Al_2O_3 and TiO_2 exceeds the total amount of the modifier oxides, vitrification is difficult. Accordingly, it is preferable that the total amount of Al_2O_3 and TiO_2 be 20 mol% or less.

The glass having the composition described above is allowed to have a low thermal expansion coefficient by increasing the content of the component SiO_2 or B_2O_3 , which is a network forming oxide, and minimizing the content of Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O , MgO , CaO , SrO , or BaO , which is a modifier oxide. In order for the glass to contain a large amount of SiO_2 or B_2O_3 , which is a network forming oxide, the total amount of SiO_2 and B_2O_3 is set at 60 mol% or more. On the other hand, in order for the glass to contain a smallest possible amount of Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O , MgO , CaO , SrO , or BaO , which is a modifier oxide, the total amount thereof is set at 20 mol% or less.

In order to obtain more uniform glass with a common melting method, it is desirable that the composition satisfy the following condition, within the composition range described above:

$$(\text{Al}_2\text{O}_3 + \text{TiO}_2) / (\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Rb}_2\text{O} + \text{Cs}_2\text{O} + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO}) \leq 0.9.$$

Moreover, from the viewpoint of both the decrease in thermal

expansion coefficient and improvement in laser processability, a particularly preferable composition satisfies the following ranges:

$$70 \leq \text{SiO}_2 + \text{B}_2\text{O}_3 \leq 79 \text{ mol\%};$$

$$10 \leq \text{TiO}_2 \leq 15 \text{ mol\%}; \text{ and}$$

5 $10 \leq \text{Na}_2\text{O} \leq 15 \text{ mol\%}.$

In this case, the thermal expansion coefficient further can decrease when the total amount of SiO_2 and B_2O_3 , which are network forming oxides, is at least 70 mol% and the amount of Na_2O , which is a modifier oxide, is 15 mol% or less.

10 Furthermore, when the content of TiO_2 , which is a component required for lowering the laser processing threshold value, is at least 10 mol%, the laser processability further can improve. However, when the content of TiO_2 is larger than that of Na_2O , which is a modifier oxide, vitrification is difficult. Accordingly, it is preferable that the content of TiO_2 be 15 mol% or
15 less.

Since the total amount of SiO_2 and B_2O_3 , which are network forming oxides, is at least 70 mol%, it is preferable that the content of Na_2O , which is a modifier oxide, be at least 10 mol%. This is intended to reduce the viscosity to be obtained at high temperatures and decrease the temperature
20 gradient of viscosity through the increase in content of the modifier oxide.

When glass absorbs laser beams, variations in glass structure or absorptance occur to cause ablation or evaporation. The glass having the aforementioned composition of the present invention requires less energy to be processed by causing the phenomenon and therefore has a low processing
25 threshold value. Furthermore, the glass for laser processing of the present invention is not modified through, for instance, an ion exchange but is allowed to have a necessary composition by melting. Accordingly, the composition of the glass is substantially uniform in the thickness direction. Hence, it is possible to carry out easily not only processing of the vicinity of
30 the glass surface but also processing of the inner part of the glass, such as, for instance, processing for making a through hole in a glass sheet. In the above, the phrase, "substantially uniform in the thickness direction", denotes that the glass composition is uniform to an extent that allows even the inner part of the glass to be laser-processed.

35 Preferably, the glass of the present invention has a thermal expansion coefficient of $100 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ or lower.

Preferably, the glass of the present invention has processing threshold

values of 60 mW or lower at a wavelength of 266 nm and 500 mW or lower at a wavelength of 355 nm as well as a thermal expansion coefficient of $100 \times 10^{-7} \text{°C}^{-1}$ or lower, where ultraviolet rays with the wavelengths of 266 nm and 355 nm of a Nd:YAG laser were used as laser beams, the laser has a frequency of 20 Hz and a pulse width of 5 to 8 nm, the laser beams are focused with a lens whose focal length is 100 mm, and the processing threshold values denote energy used at the limit of causing ablation by irradiating the glass with the laser beams.

EXAMPLES

Examples in which the present invention is used are described below, but the present invention is not limited to them.

(1) Method of Producing Glass

Raw materials were blended so that 200 g of glass was to be produced. This was put into a platinum crucible, which then was placed in a melting furnace whose temperature had been raised to about 1500°C. This was maintained for six hours while being stirred several times. Casting was carried out by pouring the glass on an iron plate. Immediately thereafter, it was placed in an annealing furnace whose temperature had been raised to about 500°C. It then was maintained at a predetermined temperature for 30 minutes and then was cooled slowly to room temperature over 16 hours. A glass block thus obtained was cut and polished by a common method. Thus a sheet-like sample of glass for laser processing with smooth surfaces was prepared.

(2) Measurement of Laser-Irradiation Processing Threshold Value

A glass substrate was processed by laser irradiation as follows using a laser irradiation device 1 shown in FIG. 1.

A laser beam 10 emitted from a laser source 12 is focused by a lens (not shown in FIG. 1) and then a glass sample 20 attached to a sample holder 22 located on a sample stage 24 is irradiated therewith. An attenuator 50 is a device for changing the level of energy of the laser beam that passes therethrough. An operation of a micrometer (not shown in FIG. 1) allows the attenuator 50 to adjust the level of energy of the laser beam 10 that passes therethrough. The glass sample 20 is irradiated with the laser beam 10 whose energy level has been adjusted by the attenuator 50.

The sample stage 24 is a stage that freely can move three-dimensionally around one axis extending in the direction parallel to the optical axis of the laser beam 10 and two axes extending in the plane

perpendicular to the optical axis of the laser beam 10. The sample stage 24 can be moved by electric signals and thereby can be controlled as predetermined.

5 The sample holder 22 can be tilted freely with respect to the direction of the optical axis of the laser beam 10. The type of the laser beam 10 can be selected from the third harmonics (whose wavelength is 355 nm) and the fourth harmonics (whose wavelength is 266 nm) of a Nd:YAG laser and laser beams of a KrF excimer laser (whose wavelength is 248 nm) by changing the laser source 12. Furthermore, a mask (not shown in FIG. 1) was placed on
10 the optical axis in the vicinity of the glass sample 20 as required, and thereby the diameter or size of the laser beam was changed.

The laser processing threshold value was measured as follows. Ultraviolet rays with wavelengths of 266 nm and 355 nm of the Nd:YAG laser were used as the laser beam 10. This laser had a pulse rate of 20 Hz and a
15 pulse width of 5 to 8 nm. The laser beam 10 was focused by a lens (not shown in FIG. 1) whose focal length was 100 mm. The glass sample 20 attached to the sample holder 22 located on the sample stage 24 was irradiated with the laser beam 10 thus focused. The irradiation time was controlled with an irradiation shutter 30 and was set at two seconds.

20 Energy of the laser beam 10 was measured with a power meter 40 placed on an optical path of the laser beam 10 in the state where the irradiation shutter 30 was closed. The sample was irradiated with laser beams whose energy level was changed variously by the attenuator 50, and the amount of energy used at the limit of causing ablation was determined,
25 which was defined as the processing threshold value.

The laser source 12 generates high energy beams. Hence, for ensuring safety, the laser source 12 can be controlled remotely. A device 14 that supplies power and cooling water to the laser source 12 is operated with a remote controller 16. The laser source 12 itself also contains a shutter
30 although it is not specifically shown in FIG. 1. This shutter also can be controlled remotely. Laser beams that have passed through the glass sample 20 are absorbed by a beam damper 18.

(3) Measurement of Thermal Expansion Coefficient

35 Measurement of the thermal expansion coefficient was carried out according to Japanese Industrial Standards, JIS R3103.

Examples in which the present invention is used are described below, but the present invention is not limited to them.

Examples 1 to 12

The compositions of glasses for laser processing of the present invention according to Examples 1 to 12 are indicated in Table 1. The compositions of respective components are within the following ranges:

- 5 a. network forming oxides (SiO_2 and B_2O_3) : 60 to 79 mol%;
- b. intermediate oxides (Al_2O_3 and TiO_2) : 5 to 20 mol%, wherein the content of TiO_2 must be 5 to 20 mol%; and
- c. modifier oxides (Li_2O , Na_2O , K_2O , MgO , CaO , SrO , and BaO): 5 to 20 mol%.

10 The glass for laser processing of the present invention consists substantially only of the compositions described above except for a very small amount of impurities.

The samples of glasses for laser processing having compositions mentioned above were irradiated with respective laser beams having wavelengths of 266 nm and 355 nm, with the irradiation energy being varied. 15 Table 1 shows the processing threshold values obtained as a result.

It can be understood that in both the cases of using the respective wavelengths, the processing threshold value decreases considerably with an increase in concentration of TiO_2 . However, the processing threshold value hardly depends on the compositions of the network forming oxides and 20 modifier oxides.

FIG. 2 shows vitrification conditions of respective compositions, with the relationship between the total amount of Al_2O_3 and TiO_2 and the amount of Na_2O being plotted with respect to various compositions tested by the inventors. It can be understood from FIG. 2 that an excessively small 25 amount of modifier oxides that are typified by Na_2O causes phase splitting and devitrification and thus prevents uniform glass from being produced. That is, as shown in FIG. 2, in order to produce uniform glass, a relationship of:

$$30 \quad \frac{(\text{Al}_2\text{O}_3 + \text{TiO}_2)}{(\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Rb}_2\text{O} + \text{Cs}_2\text{O} + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO})} \leq 0.9 \quad (1)$$

must hold.

As described above, in order to decrease the laser processing threshold value, the glass needs to contain a large amount of TiO_2 . In this case, in order to satisfy the condition of the formula (1), it is necessary to 35 increase the concentration of the modifier oxides. The increase in concentration of the modifier oxides, however, generally results in an increase in thermal expansion coefficient. Accordingly, it can be understood that the

decrease in the processing threshold value and the decrease in the thermal expansion coefficient have a trade-off relationship.

Comparative Example 1

Comparative Example 1 is a so-called soda-lime glass that is used for common window glass, for instance. The processing threshold values were determined in the same manner as in the examples. The maximum power was 1.10 W at a laser beam wavelength of 266 nm while it was 2.10 W at a laser beam wavelength of 355 nm. In both the cases, neither ablation nor evaporation occurred and thus no change was observed in the sample. Compositions having a very low concentration of TiO_2 or Al_2O_3 , which is an intermediate oxide, or containing no TiO_2 or Al_2O_3 result in extremely high processing threshold values.

Comparative Example 2

As shown in Table 1, Comparative Example 2 is a material containing TiO_2 , which is an intermediate oxide, and Na_2O , which is a modifier oxide, each of which has a high concentration exceeding 20 mol%. The processing threshold values were determined in the same manner as in the examples and were very low, specifically 15 mW and 200 mW at laser beam wavelengths of 266 nm and 355 nm, respectively. However, the glasses having compositions of the examples have thermal expansion coefficients that are lower than $100 \times 10^{-7} \text{°C}^{-1}$ while the glass having the composition of this comparative example has a thermal expansion coefficient as high as $118 \times 10^{-7} \text{°C}^{-1}$.

When the examples and comparative examples described above are taken into account, it turns out that in obtaining a glass whose thermal expansion coefficient is as low as possible and whose processing threshold value also is low, the most preferable compositions are compositions that are typified by Examples 11 and 12, i.e. compositions that satisfy the condition of the formula (1) described above and additionally are in the following ranges:

$70 \leq \text{SiO}_2 + \text{B}_2\text{O}_3 \leq 79 \text{ mol\%};$
 $10 \leq \text{TiO}_2 \leq 15 \text{ mol\%};$ and
 $10 \leq \text{Na}_2\text{O} \leq 15 \text{ mol\%}.$

Table 1

Components (mol%)	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
SiO ₂	60	60	60	60	60	60	60
B ₂ O ₃	0	0	0	0	0	0	0
TiO ₂	10	20	20	20	20	10	20
Al ₂ O ₃	10	0	0	0	0	10	0
Na ₂ O	10	20	15	15	15	15	15
Li ₂ O	0	0	5	0	0	0	0
K ₂ O	0	0	0	5	0	0	0
MgO	0	0	0	0	5	0	0
CaO	0	0	0	0	0	5	0
SrO	0	0	0	0	0	0	5
BaO	10	0	0	0	0	0	0
Total	100	100	100	100	100	100	100
Processing Threshold Value (mW)							
Wavelength: 266 nm	60	25	25	25	25	25	25
Wavelength: 355 nm	500	300	300	300	300	300	300
Thermal Expansion Coefficient (°C ⁻¹)	82	97	94	99	86	89	90

Components (mol%)	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	C. Ex. 1	C. Ex. 2
SiO ₂	60	60	60	60	65	72	37.5
B ₂ O ₃	0	0	10	10	10	0	12.5
TiO ₂	20	20	10	15	12.5	0	25
Al ₂ O ₃	0	0	0	0	0	0.9	0
Na ₂ O	15	10	10	15	12.5	12.7	25
Li ₂ O	0	0	0	0	0	0	0
K ₂ O	0	0	0	0	0	0	0
MgO	0	0	0	0	0	6	0
CaO	0	0	0	0	0	8.4	0
SrO	0	0	0	0	0	0	0
BaO	5	10	10	0	0	0	0
Total	100	100	100	100	100	100	100
Processing Threshold Value (mW)							
Wavelength: 266 nm	25	25	60	30	30	–	15
Wavelength: 355 nm	300	300	500	400	400	–	200
Thermal Expansion Coefficient (°C ⁻¹)	91	87	82	75	64	–	118

Remarks: - “Thermal Expansion Coefficient” is indicated as the value to be multiplied by 10⁻⁷.

5 - “Ex.” and “C. Ex.” denote Example and Comparative Example, respectively.

INDUSTRIAL APPLICABILITY

The present invention can provide a glass for laser processing that has a low laser processing threshold value as well as a low thermal expansion coefficient. In other words, the glass for laser processing of the present
5 invention requires less laser beam energy to be processed and is affected less by heat. Thus, the glass for laser processing can be processed more precisely.